Ask Dr. ALOHA:

Some unusual chemicals

Eric Blake, an ALOHA trainer, is developing a set of example scenarios for an upcoming training class. He decides to use a release of liquid fluorine from a tank as an example scenario. He performs the usual initial steps of an ALOHA run: first choosing location, time and date, chemical, weather conditions, and source strength options, and next entering the dimensions of a tank. He then indicates that the tank contains liquid fluorine stored at the ambient air temperature, 50°F (10°C). When he clicks **OK**, however, ALOHA displays an alert (Figure 1).

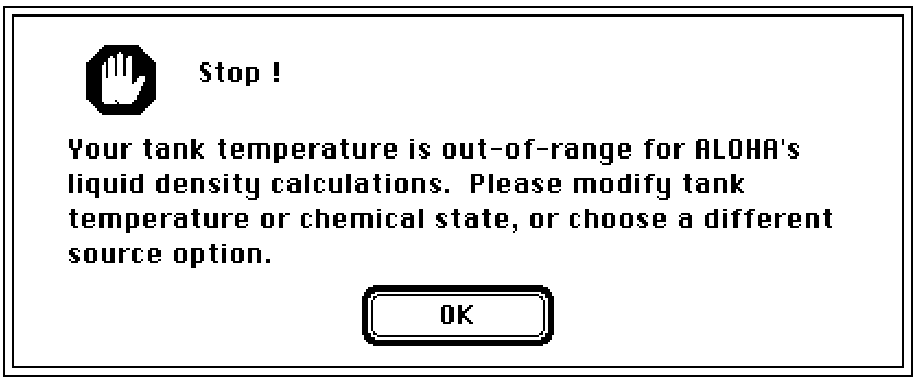


Figure 1. Alert explaining that ALOHA cannot estimate liquid density.

What's going on? Eric is not sure how to interpret this message.

<u>Unusual chemicals</u>

There are some unusual chemicals in ALOHA's chemical library. When you try to model a release of one of these chemicals, you may obtain surprising results. Let's look at two such chemicals, fluorine and acetylene, and discuss how and why you may obtain unexpected results from ALOHA when you select either chemical from the library. We'll begin with fluorine.

Fluorine has a low critical temperature

Fluorine is an example of a chemical with a very low **critical temperature**. This is the temperature above which a gas cannot be compressed to form a liquid, no matter how much pressure is exerted on it. Any gas has a critical temperature, but for most common chemicals, the critical temperature is well above common ambient temperatures. Ammonia and chlorine are typical: at room temperature, exerting pressure on either of these gases can liquefy it. In contrast, because the critical temperature of fluorine is -200°F (-129°C), this gas cannot be compressed to form a liquid at any ambient air temperature encountered on earth. It is generally stored and transported as a compressed, nonliquefied gas rather than as a pressurized liquid. ALOHA “knows” this because its chemical library contains the critical temperature of fluorine.

What does the alert mean?

Once Eric indicated that fluorine was stored as a liquid in a tank at 50°F (10°C), ALOHA tried to estimate the properties of liquid fluorine at that temperature (it uses equations and coefficients hidden away in the chemical library to estimate properties that change with temperature, such as density and vapor pressure). When it attempted to estimate fluorine's liquid density, it first checked the tank temperature of 50°F (10°C) against fluorine's critical temperature. Because this temperature is higher than the critical temperature, ALOHA recognized that the fluorine in the tank could not be a liquid. It then displayed the alert indicating that it could not estimate the liquid density of fluorine because the temperature was too high.

Other ALOHA chemicals have low critical temperatures.

Other chemicals in ALOHA's library also have critical temperatures below common air temperatures (Table 1). Like fluorine, these chemicals cannot be modeled as liquids when they are warmer than their critical temperature.

Table 1. The 15 ALOHA chemicals with the lowest critical temperatures.

NAME	Critical Temperature	
	°F	°C
HELIUM	-450.3	-268.0
DEUTERIUM	-390.6	-234.8
NEON	-379.8	-228.8
NITROGEN	-232.5	-147.0
CARBON MONOXIDE	-220.4	-140.2
FLUORINE	-200.3	-129.0
ARGON	-188.1	-122.3
OXYGEN	-181.4	-118.6
NITRIC OXIDE	-135.4	-93.0
METHANE	-116.7	-82.6
KRYPTON	-82.8	-63.8
TETRAFLUOROMETHANE	-50.2	-45.7
NITROGEN TRIFLUORIDE	-38.7	-39.3
SILICON TETRAFLUORIDE	6.5	-14.2
BORON TRIFLUORIDE	10.0	-12.3

Viewing critical temperature in ALOHA

You can view a chemical's critical temperature in ALOHA, even though this value is not displayed on the Text Summary window. To do this, choose **Chemical...** from the **SetUp** menu, click on the chemical's name to select it, click **Modify** to view the chemical's properties, then click **Critical Temperature** (Figure 2). Critical temperature is displayed in Kelvins (the Kelvin temperature scale is preferred by chemists). To then convert a value in Kelvins to degrees Celsius, subtract 273 from the value. To convert a value in degrees Celsius to degrees Fahrenheit, multiply the value by 9/5, then add 32. For example, fluorine’s critical temperature of 144 K equals 144 - 273 = -129°C. This value equals [9/5 × (-129)] + 32 = -200°F.

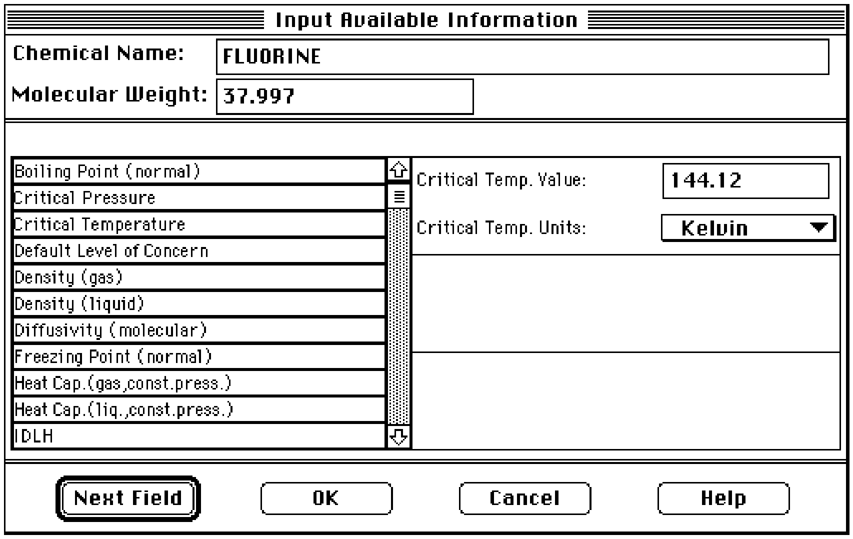


Figure 2. Fluorine’s critical temperature displayed in ALOHA.

Acetylene sublimates rather than boils

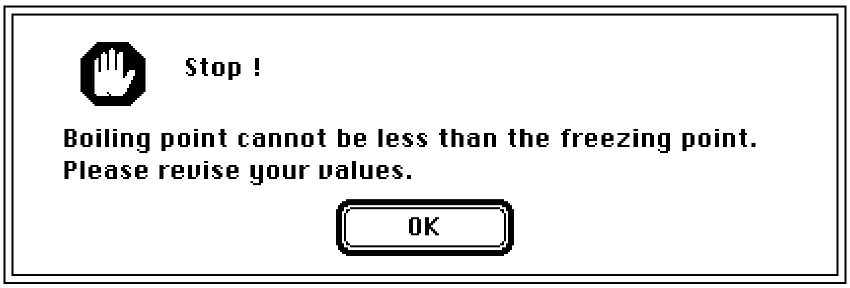
Eric next chooses acetylene from the chemical library to prepare another example scenario. He notices that ALOHA 5.2 contains values for acetylene’s freezing point and many other properties, but does not contain a value for normal boiling point (earlier versions of ALOHA contained only a value for acetylene’s molecular weight). He wonders why just one property value is missing.

What is “normal” about a boiling point?

A chemical’s boiling point changes when pressure changes; that’s why water boils at a higher temperature in Denver than in Seattle. A liquid’s **normal boiling point** is the temperature at which it boils when it is under exactly 1 atmosphere of pressure.

Acetylene does not have a normal boiling point in the usual sense because it does not form a liquid phase under only 1 atmosphere pressure. The temperature -119°F (-84°C) is often reported as acetylene’s boiling point, but this temperature is actually acetylene’s **sublimation point**. At or above this temperature, at 1 atmosphere of pressure, solid acetylene goes directly to the gas phase by a process called sublimation, rather than first becoming a liquid that then evaporates to form a gas. Acetylene sublimates rather than evaporates because it is a reluctant liquid: in liquid phase, molecules of acetylene are only very weakly attracted to each other (the stronger attraction between molecules of other liquids is what keeps those chemicals in the liquid state).

Without a value for boiling point, Eric can use only the Direct source and Gaussian dispersion options; he can't use the Tank, Puddle, or Pipe source or heavy gas dispersion options. Eric finds acetylene's boiling point in CAMEO's RIDS module, and decides to add this value to ALOHA's library. To do this, he chooses **Chemical...** from the **SetUp** menu, clicks "ACETYLENE" to select it, clicks **Modify** to view this chemical's properties, and then clicks **Boiling Point (normal)**. He then enters -119°F into the Boiling Point Value field, and clicks **OK**. To his surprise, ALOHA displays the following alert:



When he reviews these two values, he realizes that ALOHA's value for the freezing point of acetylene, -113°F (-81°C), is indeed slightly higher than the boiling point value that he obtained from CAMEO. How can something freeze at a higher temperature than it boils?

The reason is that, for technical reasons, the two properties were measured at different pressures. The boiling point was measured at a pressure of exactly 1 atmosphere, but the freezing point was measured at a slightly higher pressure (technically, at acetylene's triple point). A chemical's freezing point increases when the pressure exerted on the chemical increases.

Carbon dioxide is similar to acetylene in that it also sublimates directly from the solid to the gas phase. As with acetylene, ALOHA contains a value for carbon dioxide's freezing point, but not for its boiling point.

What can Eric do?

Because acetylene and carbon dioxide have such unusual properties, and because ALOHA doesn't account for sublimation, Eric should limit himself to using ALOHA's Direct source and Gaussian dispersion options when he selects either chemical from ALOHA's library. If he changes the freezing and boiling point values for either chemical, he will not obtain accurate results from ALOHA. In essence, he would then be modeling a different chemical than the one he selected from the library.

Confused by ALOHA's results?

Each of the vast multitude of chemicals that make up the material world exhibits a distinctive set of chemical and physical properties. Chemicals act in diverse ways and can sometimes surprise us. When ALOHA's results or alert messages confound you, consider the properties of the chemical you have selected in order to understand and resolve the problem. Check the chemical's property values in ALOHA's chemical library or in CAMEO. Talk with experts or review reference materials at your worksite or local library to find out more about the chemical.

You may wish to check the following references:

• Handbook of Toxic and Hazardous Chemicals. 1991. Sittig, M. Park Ridge, New Jersey: Noyes Data Corporation.
• Hawley's Condensed Chemical Dictionary, 12th ed. 1992. Sax, N. I., Lewis, R. J. Philadelphia: Van Nostrand Reinhold.
• The Merck Index, 11th ed. 1989. Budaveri, S., ed. Rahway, NJ: Merck.

If you have access to the Internet, you can find information about many chemicals there. To view factsheets describing many hazardous chemicals, try http://www.cais.com/nsc/ehc/chm/chem35.html at the National Safety Council, gopher://ecosys.drdr.virginia.edu/11/library/gen/toxics at the University of Virginia, or http://atsdr1.atsdr.cdc.gov:8080/toxfaq.html at the Agency for Toxic Substances and Disease Registry. To access a keyword-searchable MSDS database, try http://research.nwfsc.noaa.gov/msds.html at NOAA.

As you review the information you've collected, ask yourself questions about the chemical: Is it typically stored as a liquid or gas? Does it sublimate or evaporate? Does it freeze or boil at an unusually high or low temperature? Is its vapor pressure very high (so that it evaporates quickly) or very low (so that under some conditions it may not even be an air hazard)? Such information can help you to better understand why ALOHA has made an unusual prediction—or has refused to make a prediction. It also can help you to verify that ALOHA is making realistic computations. Never use ALOHA or any other model without also using your common sense, knowledge, and experience. Whenever necessary, do a little research to better understand the results you obtain.

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